

V.13 A High Temperature Electrochemical Energy Storage System Based on Sodium Beta Alumina Solid Electrolyte (BASE)

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Objectives

Phase I:

- To synthesize planar, thin, strong BASE using a patented vapor phase process.
- To fabricate metal end caps and the associated hardware for the construction of planar BASE-based electrochemical energy storage systems.
- To construct electrochemical cells comprising of sodium anode, BASE, and selected cathodes.
- To electrochemically test cells (discharge-charge) over a range of temperatures and up to the highest possible depths of discharge.
- To conduct theoretical analysis of the electrochemical energy storage system from the standpoint of maximum possible capacity, efficiency, and integrability with power generation systems.

Phase II:

- To construct a planar stack of 10 Na/BASE/optimized cathode cells.
- To operate a stack for a minimum of 100 charge-discharge cycles.
- To thermally cycle the stack between the operating temperature and room temperature.
- To disassemble the stack and conduct post-mortem analysis.

Approach

- To fabricate BASE discs by the method of die pressing or tape casting and BASE tubes by the method of slip casting using a vapor phase process.
- To investigate the effect of microstructure on the kinetics of conversion.

- To fabricate BASE discs with porous BASE surface layers for enhanced electro catalysis.
- To measure the conductivity of BASE tubes by assembling a symmetric cell with a zinc chloride-sodium chloride eutectic mixture.
- To conduct ion exchange experiments in prospective cathodes of ZnCl_2 , SnCl_2 , and SnI_4 .
- To construct tubular and planar electrochemical cells that could be assembled in three different states: discharged state, charged state, and partially charged at eutectic composition.
- To conduct experiments to test the electrochemical working of tubular cells and to analyze the voltage response of the charge-discharge cycles.
- To construct planar cells and to test the electrochemical working of the same by analyzing the voltage response of the charge-discharge cycles.
- To conduct several freeze-thaw cycles on the planar cells and to test the performance of the same after undergoing the thermal cycles.
- Assemble a two cell planar stack and test.
- To conduct electrochemical tests in an aqueous media: Cu/Zn couple.
- To assemble a five cell stack.

Accomplishments

- BASE discs were successfully fabricated by tape casting, sintering and vapor phase treatment.
- BASE tubes were successfully fabricated by slip casting, sintering and vapor phase treatment.
- α -alumina + yttria-stabilized zirconia (YSZ) samples of differing grain sizes were fabricated by varying sintering temperature/time.
- Preliminary work on the kinetics of conversion was conducted.
- Electrochemical cells were designed, constructed, and tested.
- No incorporation of zinc within the BASE structure was observed, suggesting that BASE is stable in the battery environment. No incorporation of Sn^{4+} was observed suggesting BASE is stable in Sn^{4+} salts. However, ion exchange did occur in SnCl_2 , indicating BASE is not stable in the presence of Sn^{2+} salts.
- Planar cells were designed, assembled and successfully tested. Cells were subjected to several charge-discharge and freeze-thaw cycles.
- Freeze-thawing of planar cells were done a couple of times followed by several charge-discharge cycles

without the failure of electrolyte. These tests were conducted at an operating temperature of 350°C. Cells were also tested at 425°C.

- A two cell planar stack was successfully discharged.
- A five cell stack has been assembled.

Future Directions

- To test the five cell stack.
- To investigate additional cathodes. They include CuCl_2 , SnI_4 , and AgCl .
- To incorporate high conductivity BASE with porous surface layers into cells.
- To construct a 10-cell, 200 Wh (100 W with 2 hour discharge) stack with high specific energy and high specific power.
- Integration of the high temperature energy storage system based on BASE with a power generation system such as a solid oxide fuel cell (SOFC).

Introduction

The demand for electricity varies depending upon the time of the day: low demand during night and high demand during day. All power plants are designed for peak power which leads to the underutilization of excess capacity during off peak periods. One of the main reasons for the emergence of electrochemical energy storage devices such as batteries is that power plants can be designed for average demand. This will augment the capacity of power plants as the excess energy during off peak periods will be stored for use later during high peak demands. This strategy is expected to lower the capital cost. In high temperature batteries, the most advanced batteries are Na-S. NGK in Japan has demonstrated 8 MW (64 MWh – 8 hour discharge) Na-S batteries (NAS), connected to the local grid for load leveling. The roundtrip efficiency of the NAS battery is ~90%. Other batteries using BASE currently under development include the ZEBRA battery which utilizes NiCl_2 or FeCl_2 as the cathode.

Both the NAS and ZEBRA batteries use conventional BASE, which is not strong and is not water-resistant. It needs to be stored in dry atmospheres before incorporating it into batteries. The corrosive nature of the cathode (sulfur or NiCl_2) necessitates the use of tubular geometry, to minimize seal area. In the NAS battery, containers are protected by an expensive protective coating. Also, expensive graphite is required in the cathode. In the ZEBRA battery, to minimize corrosion, the cathode is placed inside the BASE tube. This lowers the specific energy and specific power. It is not possible with either of the two batteries to construct

planar cells. The main objective of this work is to use a high strength vapor phase processed BASE (patented process) to make planar cells, and use alternate cathodes to increase both specific energy and specific power.

Approach

BASE discs were fabricated using the method of tape casting and die-pressing. For tape-casting, the dispersant used was KD1. BASE tubes were fabricated by the method of slip casting with Darvan C as the deflocculent. The conductivity of the BASE tubes was measured by assembling symmetric cells. Ion exchange experiments were conducted in molten ZnCl_2 , SnCl_2 , and SnI_4 for up to 24 hours. The objective was to determine if Na^+ can be replaced by Zn^{2+} , Sn^{2+} , and Sn^{4+} ions. Na/BASE/ ZnCl_2 cells were assembled in the fully charged, fully discharged, and partially charged-discharged states. Steel wool was used in both the cathode and the anode compartments. The cells were operated up to 425°C - the temperature at which Zn is in a molten state. Samples of α -alumina + zirconia were die pressed and sintered at various temperatures, ranging between 1,500 and 1,800°C and up to 4 hours. The objective was to vary the grain size. Subsequently, samples were packed in BASE powder and heated to 1,450°C. The conversion thickness was measured as a function of time. This yielded the conversion rate. A two cell planar stack of Na/BASE/ ZnCl_2 + NaCl + Zn was constructed and tested. A five cell stack has been assembled. Disc samples of BASE with porous surface BASE layers were fabricated. The objective was to determine if porous surface layers lower cell resistance. Preliminary experiments were conducted in aqueous media by constructing electrochemical cells of the type $\text{Cu} + \text{CuCl}_2 + \text{NaCl/BASE/Zn} + \text{ZnCl}_2 + \text{NaCl}$. The cells were subjected to numerous charge-discharge cycles.

Results

1. Several BASE discs and tubes were fabricated. Figure 1(a) is a photograph of the BASE discs. Figure 1(b) is a photograph of a BASE tube.
2. The mechanism of α -alumina + zirconia conversion into BASE + zirconia was investigated. The mechanism involves coupled transport of O^{2-} ions through zirconia and Na^+ ions through BASE. The kinetics were noted to be linear in time. Figure 2(a) shows a schematic of the conversion process. Figure 2(b) shows plots of conversion thickness vs. time at various temperatures.
3. Fabrication of α -alumina + YSZ of differing grain sizes by varying sintering conditions was conducted. Figure 3(a) shows a scanning electron microscope (SEM) micrograph of a sample sintered at 1,500°C for 1 hour. The grain size is ~0.5 μm .

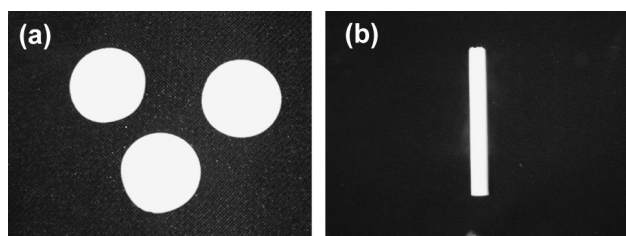


FIGURE 1. (a) A Photograph of BASE Discs and (b) a Photograph of a BASE Tube

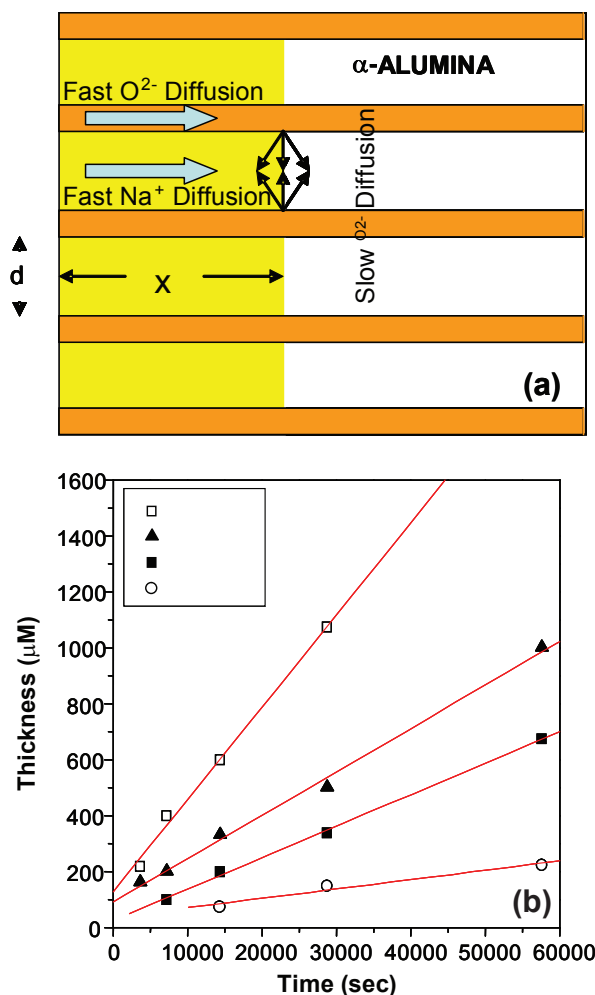


FIGURE 2. (a) A Schematic Showing the Mechanism of Conversion and (b) Experimental Data on Conversion Kinetics

The conversion rate was $\sim 0.23 \mu\text{m/s}$. Figure 3(b) shows a SEM micrograph of a sample sintered at $1,600^\circ\text{C}$ for 4 hours. The grain size is $\sim 1.24 \mu\text{m}$. The conversion rate was $\sim 0.12 \mu\text{m/s}$.

- No ion exchange occurred in ZnCl_2 . Figure 4(a) shows an energy dispersive spectroscopy (EDS) trace. Ion exchange did occur in SnCl_2 . Figure 4(b) shows an EDS trace.

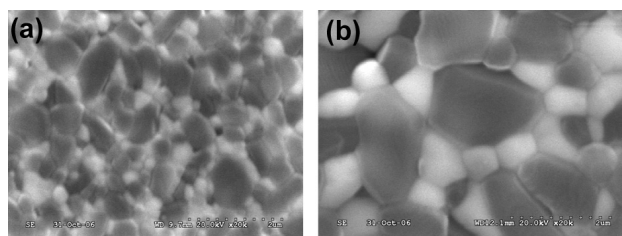


FIGURE 3. (a) Microstructure of α -alumina + Zirconia Sintered at $1,500^\circ\text{C}/1$ Hour and (b) Microstructure of α -alumina + Zirconia Sintered at $1,600^\circ\text{C}/4$ Hours

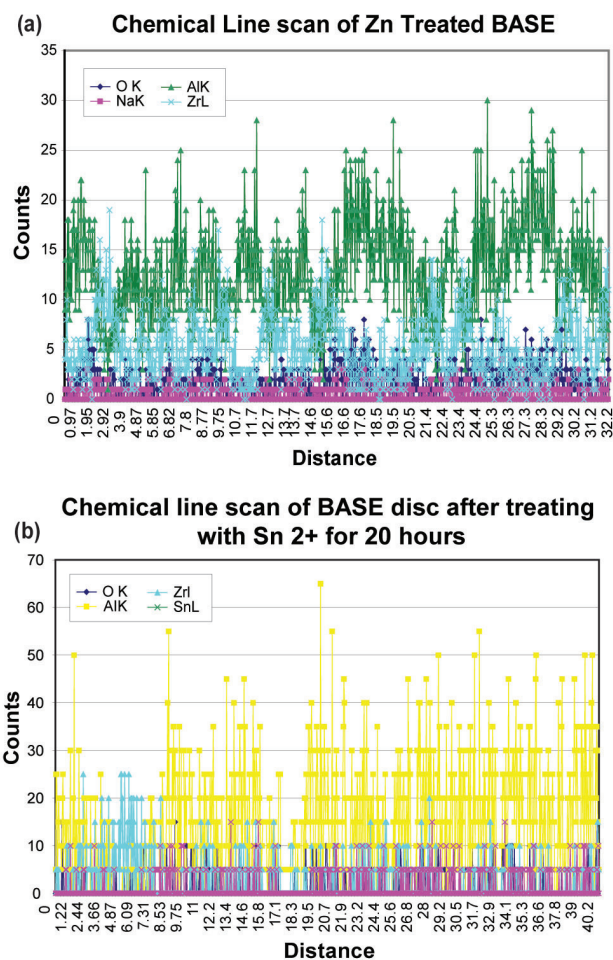


FIGURE 4. (a) EDS Trace of a Sample Treated in Molten ZnCl_2 and (b) EDS Trace of a Sample Treated in SnCl_2

- Planar $\text{Na}/\text{BASE}/\text{Zn} + \text{ZnCl}_2 + \text{NaCl}$ cells were made. Figure 5 shows components of a planar cell.
- The cell was subjected to several charge-discharge cycles and freeze-thaw cycles. Figure 6 shows the results of testing at 425°C which is above the melting point of zinc.
- A five cell stack has been assembled. Figure 7 shows a photograph of a five cell stack.

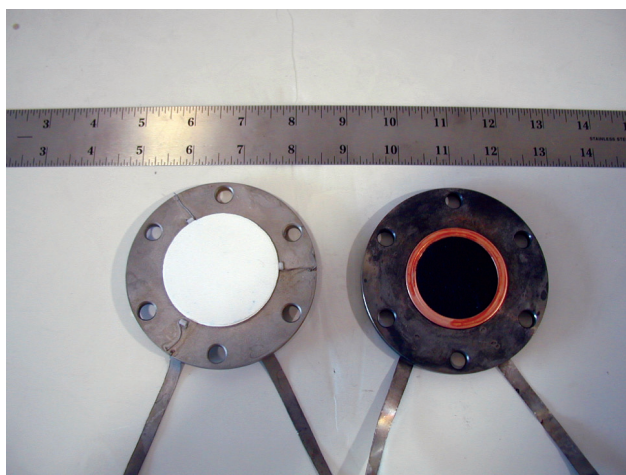


FIGURE 5. Components of a Planar Cell

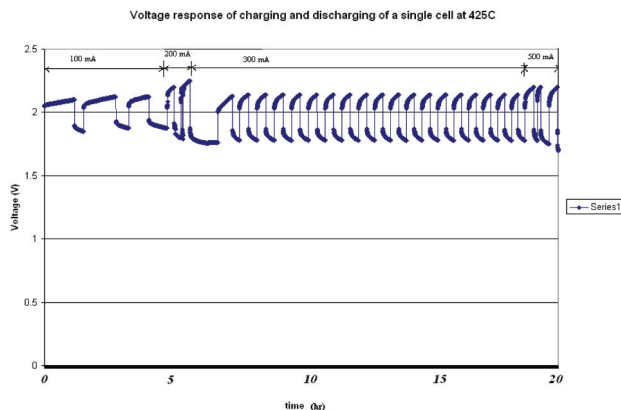


FIGURE 6. Results of Charge-Discharge at 425°C

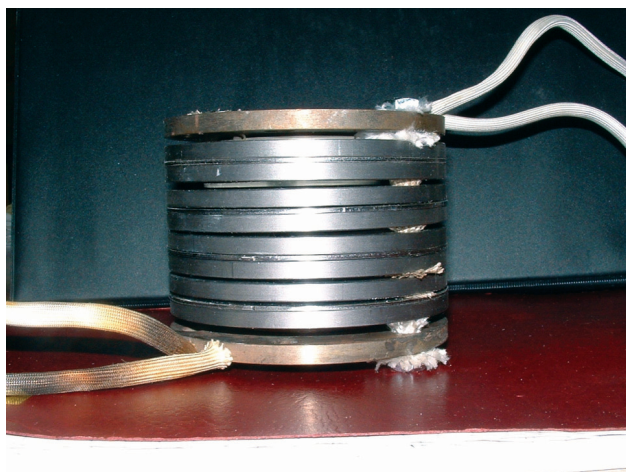


FIGURE 7. A Photograph of a Five Cell Stack

8. BASE samples with porous surface layers exhibited half the resistance of BASE without porous surface layers.

Conclusions

1. Thin BASE discs were fabricated by tape casting and die-pressing and BASE tubes were successfully made by slip casting.
2. Samples of BASE with different grain sizes were made. It is expected that samples with larger grain size will exhibit greater conductivity.
3. The conversion kinetics were linear. This suggests the kinetics to be interface controlled, where interface control arises due to diffusion parallel to the reaction front.
4. No ion exchange occurred in ZnCl_2 and SnI_4 . Thus, both of these are viable cathodes.
5. Electrochemical cells were successfully charge/discharged and subjected to freeze-thaw cycling. $\text{Na/BASE/Zn} + \text{ZnCl}_2 + \text{NaCl}$ could be successfully operated at a high temperature (425°C), indicating it should be possible to integrate with an SOFC as a hybrid unit.
6. Planar cell stacks could be assembled.